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Specification as originally filed, with Application for Patent Serial No: **2,389,939**, on June 25, 2002, by **ALICJA ZALUSKA and LESZEK ZALUSKI**, for "New Type of Catalytic Materials Based on Active Metal-Hydrogen-Electronegative Element Complexes for Reactions Involving Hydrogen Transfer".

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1. TITLE:

"New type of catalytic materials based on active metal-hydrogen-electronegative element complexes for reactions involving hydrogen transfer"

2. FIELD OF THE INVENTION:

The invention relates to new catalytic materials of specific composition and molecular structure, which are able to catalyze and improve efficiency of chemical reactions involving hydrogen transfer. The invention also relates to the production method of these catalytic complexes, and their use to facilitate the hydrogen-transfer reactions, i.e. to improve the reaction's efficiency and rate, or to lower the temperature of the reaction.

3. BACKGROUND OF THE PRIOR ART

Many chemical reactions in both inorganic and organic chemistry involve relocation of hydrogen atoms, ions (protons), or molecules, which need to be transferred from one chemical molecule to another molecule, or exchanged with other atoms, ions or radicals in the reaction route. Amongst many such reactions, the most common types are: hydrogenation and dehydrogenation, reduction/oxidation, various types of reactions involving organic compounds, electrochemical reactions, and reactions in all types of fuel cells. All these reactions may exhibit a wide spectrum of various types of chemical bonding and various underlying atomic-scale mechanisms, as well as different nature of atomic interactions. In all of them, there is however one universal feature that controls the rate and efficiency of these reactions, i.e. the effectiveness of hydrogen relocation. In the course of these reactions, the events of hydrogen transfer or exchange occur repeatedly and improving the efficiency of hydrogen relocation is the main

challenge for many chemical technologies. In the most effective way, the reactions with hydrogen transfer can be facilitated by catalysis. The ultimate role of catalysts is to promote atomic-scale processes of hydrogen transfer or exchange (by lowering the activation energy connected with hydrogen relocation). In most cases, in the absence of the catalysts the chemical reaction would either not occur at all, or would take place with much lower efficiencies, rates, or at higher temperatures.

The general field of catalysis (which became one of the critical factors for the chemical technologies) is at present relatively wide and well developed, with a large number of various catalytic materials being investigated and used.

In general, there are two main categories of catalysts: heterogeneous and homogeneous. Homogeneous catalysts are in the same phase as the basic reactants, and heterogeneous catalysts are in the different phase, for example: solid catalysts in the gaseous reactions. The development and current understanding of catalysis allows us to distinguish two essential catalytic mechanisms, i.e. acidic catalysis and basic catalysis, where reactants act either as bases toward catalysts which in turn act as acids, or as acids toward basic catalysts. Amongst many types of basic catalysts, the following are the most common: (H. Hattori "Heterogeneous Basic Catalysts", Chem. Rev. 1995, 95, 537)

- Single component metal oxides (e.g. alkaline earth oxides)
- Zeolites
- Supported alkali metal ions (e.g. alkali metals on alumina)
- Clay minerals
- Non-oxide catalysts (e.g. KF supported on alumina)

For acidic catalysis, the following catalytic materials are being commonly used (A. Corma "Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon reactions", Chem. Rev. 1995, 95, 559):

- Solid acid catalysts (e.g. amorphous silica-alumina and aluminum phosphate)
- Zeolites and zeotypes
- Heteropoly acids
- Sulfated metal oxides.

The simplest catalysts are single-phase materials, such as metals, oxides, sulfides, carbides, borides and nitrides. Metal particles are among the most important catalysts, being used on a large scale for refining petroleum, conversion of automobile exhaust, hydrogenation of carbon monoxide, hydrogenation of fats and many other processes. Multiphase catalysts usually consist of an active phase (e.g. metal particles or clusters) dispersed on a carrier (support). It is generally assumed that metal particles act most probably as active centers for the hydrogen dissociation, but the role of the support is so far still not fully understood. In practice the metal is often expensive (for example Pt) and may constitute only about 1 wt.% of the catalytic material, being applied in a finely dispersed form as particles on a high-area porous metal oxide support (B.C.Gates "Supported Metal Clusters: Synthesis, Structure, and Catalysis", Chem. Rev. 1995, 95, 511). Supported metal clusters are synthesized through organometallic chemistry on surfaces, gas-phase cluster chemistry and special preparation of zeolite cages. The preparation methods commonly use techniques from preparative chemistry, such as precipitation, hydrolysis, and thermal decomposition. These processes involve mixing of solutions, blending of solids, filtration, drying, calcinations, granulation, extrusion (J.E. Schwarz et al. "Methods of Preparation of Catalytic Materials" Chem. Rev. 1995, 95 477).

Although generally catalysis is one of the most important fields of chemical technology, it is still far from being accomplished. Most catalysts are difficult to fabricate and the production process involves a sequence of several, complex steps (as mentioned above), many of which are still not completely understood (J.E. Schwarz et al. "Methods of Preparation of Catalytic Materials" Chem. Rev. 1995, 95 477). As a result, subtle changes in the preparative details may result in dramatic alteration in the properties of the final catalysts, which may thus become ineffective. Especially, the manner in which the active component of the catalyst is introduced onto a support, as well as the nature of the interaction between the active element and the carrier, could be of critical importance. Another crucial challenge in the preparation of catalysts is the ability to prepare these materials with sufficiently high surface area. Also, most of the multicomponent metal oxides

require high-temperature treatment (exceeding 1000°C, as for alumina-based oxides), which is a significant technical drawback.

Another problem is that catalytic materials usually require "activation" i.e. some special treatment, before they could become active as catalysts, for example high-temperature annealing in vacuum or hydrogen atmosphere. Even then, however, in certain cases, the effect of annealing in hydrogen can indeed improve the catalyst's activity, but for other catalytic materials, the same treatment can actually have an adversary effect. Although the experimental data suggest that different catalytic supports lead to different effects of hydrogen treatment, these problems are still unresolved (B.C. Gates "Supported Metal Clusters: Synthesis, Structure, and Catalysis", Chem. Rev. 1995, 95, 511). Moreover, most catalysts become rapidly deactivated when exposed to air. They should be therefore handled under protective atmosphere, and pretreated at high temperatures after exposures to air in order to regain their catalytic properties.

All the above disadvantages of conventional catalytic materials cause continuous efforts to develop new, inexpensive materials with catalytic properties suitable for reactions involving hydrogen transfer, and to develop novel methods of their preparation.
The invention presents a practical and cost-efficient solution to this problem, by introducing a new type of catalytic materials, their manufacture and use as catalysts in chemical reactions.

3. SUMMARY OF THE INVENTION

The invention concerns reactions involving transfer of hydrogen, i.e. relocation of hydrogen atoms, ions (protons), or molecules. In these reactions, hydrogen needs to be transferred from one chemical molecule to another molecule, or exchanged with other atoms, ions or radicals in the reaction route. All these reactions require

that the migration or exchange of hydrogen atoms occur rapidly and easily, which in most reactions cannot be accomplished without a special catalyst.

According to the invention, new complex catalytic materials were developed, with specific structure and atom arrangement, exhibiting outstanding efficiency in enabling or improving hydrogen transfer in the above reactions, mainly through lowering the activation energy of hydrogen relocation or exchange.

The invention emphasizes a novel concept of the special interatomic interactions between the reactants and the catalyst, based on new atomic coordination in the catalytic materials. In contrast to the conventional catalysts, the new catalytic complexes do not consist (neither entirely nor in part) of any of the catalysts listed in the previous section, and more specifically, they are not constituted of metal particles, oxides and supports, or any other types of conventional catalytic materials. Specifically, instead of metallic powders or metal oxides (either single-component or multi-component), which commonly constitute the main active component of the conventional catalytic systems, the new catalyst exhibits a very specific, unique atomic configuration and structure, which in consequence give the extraordinary catalytic properties.

The complex compound of the invention consists of three (and optionally four) essential components, assembled in a distinctive way:

1. atoms of electronegative elements (E) – at least one of the group of: O, F, N, Cl, S, P, C, and also Te, I, or other complexes, or radicals being able to form under certain conditions a bond with hydrogen
2. hydrogen atom (or atoms) (H)
3. metal or metalloid component (M) - at least one metal or metalloid, being able to form hydrides, either stable or unstable, of the group of: Li, Na, K, Be, Mg, Ca, Y, Sc, Ti, Zr, Hf, V, Nb, Ta, Pt, Pd, Ru, Rh, Ge, Ga, In, La, Ce, Pr, Nd, Dy, Al, Si, B,
4. optionally: another metal component (M1) - at least one metal of the group of: Cr, Mo, W, Mn, Fe, Co, Ir, Ni, Cu, Ag, Au, Zn, Sn, Pb, Sb, Bi.

The key feature of the invention is that the above components are assembled in the following, unique manner in the catalytic complex:

$$E - H - (M+M1)$$

where:

E – electronegative component

H – hydrogen

M – metal or metalloid component

M1 – optional other metal component.

This formula represents the fundamental requirement that the electronegative element has to be coordinated with the metallic component **through** the hydrogen atom, but not directly. This feature is of the most significance, because it differentiates the complex compounds according to the invention from all types of oxides, chlorides, nitrides, sulfides, fluorides, carbides and similar compounds involving bonding between M (metal or metalloid component) and E – electronegative component. In the same way, for example hydrous oxides are also different from the new catalysts (although they may contain both E and hydrogen atoms) because their atomic arrangement is based on the direct metal-oxygen bonding, but not metal-hydrogen bonding.

It has to be stressed that the unique atomic configuration of the invention most probably does not involve typical atomic bonding between the components, which are normally formed in the usual preparatory techniques, but a specific, active coordination of the components, which is based (at least in part) on the "hydrogen bridging" phenomenon.

The specific atomic arrangement of the invention is also obviously distinct from compounds containing hydroxyl groups ($^{-}$OH groups), in which the hydroxyl group is connected to the metallic or other element or group through a single bond with oxygen (e.g. in hydroxides: M-OH), but not through the hydrogen atom. On the other hand, in acids, the electronegative elements are bonded to hydrogen, but not to metals through hydrogen, which makes them also different from the atomic coordination of the invention.

The key of the invention is also the fact that usual methods of the synthesis of compounds containing metal, hydrogen and the electronegative element (e.g. oxygen) result normally in the formation of known, common compounds, for example hydroxides. When a metal reacts with water (for example Na or Mg), a hydroxide is formed in a usual reaction (e.g. NaOH or $Mg(OH)_2$). In these conventional chemical reactions it is practically impossible to reverse the atomic arrangement of O and H in such a way that instead of the hydroxyl group bonded to the metal, hydrogen forms an active bridge between the metal and oxygen. However, in the practical aspect of the invention, a catalytic complex according to the invention's formula can be produced in a simple, efficient process, as described below in detail. The crucial condition for the formation of these specific catalytic complexes is that the metallic component <u>is not</u> exposed simultaneously and directly to the electronegative element and hydrogen (as in direct reactions which involve formation of the hydroxyl group). Instead, the process is carried out in a specific, controlled manner, resulting in the formation of the desired atom arrangement. In other words, in the process of the invention the reaction between H and O (or other electronegative element) is not allowed to proceed, unless the metallic component is already bonded to hydrogen. In this way, the final product is neither an oxide nor a hydride, nor a hydroxide. Instead, the required complex is formed, containing both hydrogen and oxygen (or other electronegative element), being arranged in the above, unique configuration. The closest description of this special complex is probably "oxidized hydride", "fluorized hydride" or "chlorinated hydride" etc., but neither a hydrous oxide nor any of the analogous compounds. Also, it has to be stressed again that this configuration should not be understood in terms of conventional atomic bonding, but rather as a special type of hydrogen bridging.

Within the scope of the invention, many possible processes are effective in producing the catalytic materials according to the above formula. The optimum procedure obviously depends on the specific chemical properties of the metallic component, in particular on its respective affinity to hydrogen and to the electronegative element (such as oxygen, fluorine, nitrogen, chlorine, sulphur, carbon etc). Therefore, a number of reaction routes can be applied as described

below, which can be extended within the same general concept to many variations and modifications.

Ultimately, the metallic component can be conveniently used as a starting material, (a single metal, a metal alloy, or a homogeneous or inhomogeneous combination of two or more metallic elements). Alternatively, the starting material could be a hydrided metallic component, i.e. the metallic component previously exposed to hydrogen.

There are three general routes for the process of the formation of new catalytic materials:

1. **a solid-gas reaction**

The solid metallic component is exposed to hydrogen and oxygen (or chlorine, or fluorine, or nitrogen) in the gas phase. However, instead of applying the gas mixture, a sequence of gas admission steps is applied. The process involves, for example, exposure to hydrogen under certain conditions of temperature and pressure, which results in hydrogen adsorption or absorption, through the metal surface. It is then followed by the admission of the other gas under certain conditions of temperature and pressure. In order to finally form the required atomic configuration according to the invention, either complete oxidation or complete reduction of the metallic component should be avoided in the process, in order for both basic components (hydrogen and the electronegative element) to be present in the metallic complex.

In order to improve and control the reactivity of the metallic component and the efficiency of the formation of the catalytic complexes, the reaction is performed preferably in a ball mill. In this process, the milling of the metallic powder proceeds consecutively under the atmosphere of hydrogen, followed by ball milling under oxygen (or chlorine, or other gases), performed in a precisely defined sequence of conditions. As indicated above, instead of a metallic component, an already hydrogenated metallic component can be used as a starting material, or even a previously formed hydride (or a mixture of hydrides).

2. solid-liquid reaction

The reaction of the metallic component with hydrogen and electronegative element involves a liquid medium, supplying either hydrogen or the electronegative element, or both of them. The simplest example of such process is the use of water, which contains both hydrogen and oxygen. Normally, a reaction of water with metals leads to the formation of hydroxides, but under the specific conditions of this invention, the process can lead to the formation of the required catalytic complexes. One key requirement is that the molecule of water is physically broken before reacting with the metallic component. This can be accomplished in a high-energy ball mill. As a result of the intense ball milling, hydrogen from the water molecules can bind with the metallic element, being subsequently followed by the incorporation of the electronegative element (oxygen) into the complex. Some evolution of hydrogen gas can also be detected. The crystallographic structure of the solid precipitate formed in this process is totally distinct from the structure of the respective hydroxide, which would form in the usual reaction. Precisely determined proportions of the amount of the metallic component and water, subjected to intense ball milling, can produce outstanding catalytic complexes in a very simple and inexpensive process. In our study, a selection of catalytic complexes was developed through a ball milling process using water, which acted as an oxygen and hydrogen carrier. As above, the starting material can be either in the metallic state, or in the already hydrided state. Similarly, a variety of other oxygen- and hydrogen-bearing liquids can be used, for example hydrogen peroxide (alone or in various solutions with water). Other various liquids or solutions of peroxides, bases, alkoxides or acids can be also used as reactants in the carefully designed process. In particular, a wide selection of organic liquids can be very effective, of which alcohols or glycerins are extremely efficient. In the case of organic liquids, the presence of carbon atoms is not adversarial, but improves the properties of the final catalysts, possibly acting as the second electronegative element in the complex. Other possible liquids are liquid hydrocarbons, chlorides, fluorides, etc.

3. solid-solid reactions

In this case, at least one of the components among hydrogen and the electronegative element is introduced in the form of a solid compound, for example a solid hydrocarbon, such as solid polymer, or oxide, chloride, fluoride, sulfide, carbide, telluride or iodide, alkoxide etc. Hydrides, hydroxides, solid acids, bases, or other compounds can be also used as hydrogen- and electronegative element- sources. These compounds can also contain metals or metalloids either different or the same as the main (M + M1) components. As above, the most effective way of producing the required catalytic complexes is to use a high-energy ball mill, providing a solid-state reaction between the metallic element (either previously hydrogenated or not) and the solid source of the electronegative element and hydrogen. The hydrogen source (for example a solid hydrocarbon, a hydride) can be at first introduced to the metallic element, followed by adding in the second stage the electronegative element source, for example an oxide. In a one-stage process, a specific combination of solid carriers supplying the hydrogen and/or the electronegative element can be used, for example a mixture of an oxide and a hydride, a mixture of alkoxides, oxides, chlorides, etc. A specific example of the process in the solid state is when a solidified source of hydrogen and of the electronegative element is introduced, for example water in the form of ice, which can also be performed at adequately low temperatures.

4. variations of the above processes

All above types of the manufacturing process can be used in various combinations, depending on the specific formula of the catalytic complex. For example, solid hydride can be milled under gaseous oxygen, liquid fluoride can be milled with a hydrogenated metallic alloy, or gaseous hydrogenation can be performed in a ball mill, then followed by ball milling with water, or with a solid hydrocarbon.

In the above methods of the catalysts production, the most effective (although not exclusive) technique is high-energy ball milling, which allows easy and efficient formation of the required catalytic complexes. However, the technique allows also extending the process onto additional steps, which include catalyst distribution on a support or on the reagent's surface (the reagent in the reaction which is to be catalyzed by the catalytic complex). The basic difference between the support and the reagent is such that the reagent takes part directly in the reaction involving hydrogen transport, and the support is a neutral medium which carries the catalyst and facilitates handling.

In the reduction to practice, the complete process of the catalyst preparation involves the following:

a. a specific process as described in one of the above four types of the catalyst formation
b. a supplementary stage, which involves distributing the catalyst on a support or the reagent (or reagents), preferably also in a ball mill.

The supplementary stage can be added either simultaneously or in steps. The simultaneous process means in practice that all components according to the invention are introduced to the ball mill simultaneously with the support or the reagent. In this way, the formation of the catalytic complex proceeds concurrently with refining the support or the reagent, and in parallel to the proper distribution of the catalyst. In the stepwise method, at least two stages of the process are used (each of them could be performed in the ball mill, but not necessarily), and in each of them the appropriate components are added, according to the above procedures. In this case the support or the reagent (or reagents) are introduced in one of the steps.

As a result of this fabrication process, the final product contains the catalytic material according to the invention, evenly distributed on the reagent or support, exhibiting sufficiently with high surface area and proper granulation.

In our experiments, we used all types of the above methods to produce catalytic compounds of the new generation. The efficiency of these compounds as catalysts for reactions involving hydrogen transfer was determined for a variety of reaction types, with outstanding results.

The new catalysts are able to facilitate or enable many reactions which depend on the efficiency of hydrogen relocation or exchange, and specifically:

- hydrogenation and dehydrogenation of a wide spectrum of compounds, including simple and complex metal hydrides, hydrocarbons and various organic compounds, reforming of hydrocarbons, alcohols, polymerization, cracking, hydrolysis etc.
- electrochemical reactions, including anodic and cathodic reactions, electrolysis of water and salts,
- reactions in fuel cells,
- reduction/oxidation reactions

The above reactions are only selected examples of various chemical reactions, in which the unique potential of the new catalysts can be exploited. The greatest prospect for the new catalysts lies in the possibility to directly design a specific composition of the catalyst in order to achieve the most efficient performance in the particular chemical reaction. This is ensured by the flexibility of the manufacturing process, which allows us to introduce almost any desired element or alloy into the complex arrangement according to the invention's formula.

The key point of the invention is that the outstanding catalytic properties can be obtained only when a specific hetero-complex is formed, as described above. Our extended study of a wide selection of the new catalysts showed indeed the enormous potential of this type of catalytic complexes for many chemical reactions.

The most striking practical property of the new catalysts is also that they do not deteriorate upon exposure to air or moisture, or after prolonged storage. For example, they can be insensitive to oxidation, since oxidation may be part of the preparation process. After fabrication, the new catalysts are already in their final, active state, with no need for further activation, high temperature annealing, or any kind of preparation/reduction process. The catalysts can be stored indefinitely without any loss of their activity and structure, even without protective atmosphere.